

COAL LIQUEFACTION IN AMINE SYSTEMS

F. Kazimi, W.Y. Chen, J.K. Chen, R.R. Whitney and B. Zimny

Gulf South Research Institute, P. O. Box 26518, New Orleans, LA 70186

I. INTRODUCTION

In developing a third generation coal liquefaction technology, reaction severity, a critical cost factor, must be minimized to make the process economically competitive with petroleum refining. Accordingly there is an incentive for the development of lower severity processes which could significantly reduce conversion costs.

The novelty of the process we are developing arises from both the liquefaction solvent selection and the design of liquefaction conditions. Low molecular weight nitrogen compounds were selected for liquefaction solvents in accordance with recent attention on the high dissolution power of nitrogen heterocycles in coal liquefaction. An excellent review of the role of these nucleophilic solvents was reported by Atherton and Kulik at the AIChE Annual Meeting in 1982. In a separate approach, supercritical fluid technology was also applied to coal liquefaction to enhance solubility of coal-derived products, minimize mass transfer limitation and, therefore, reduce process severity (Williams, 1981). The low molecular weight solvents chosen for use in the present study allowed liquefaction to be performed at supercritical solvent conditions while maintaining operating temperatures well below the most commonly used liquefaction temperature (400°C). These design criteria were applied to achieve high conversion at mild conditions.

In our first year of the study, complete dissolution of two low rank coals in amine was achieved at temperatures below 300°C (Chen and Kazimi, 1984). This level of conversion in a single stage operation at such mild conditions is strikingly higher than any other reported organic dissolution of coal at equivalent temperatures. In this paper, we report our continuing efforts to develop a coal liquefaction process using amines. The effects of processing variables, solvent property and coal rank on coal conversion have been examined. Further, the product quality, solvent removal from products and chemical recovery of the solvent are discussed.

II. EXPERIMENTAL

A. Liquefaction

Three different systems were used for liquefaction of the coal samples. The slow heating tubing bomb system was described in an earlier paper (Chen and Kazimi, 1984). The Parr bomb, used for chemical conversion of incorporated solvent, is described in the next section. A second tubing bomb system which provides rapid heating, and therefore isothermal kinetic study, is shown in Figure 1. Approximately 1 g of coal sample was placed in the upper end of the vertical part of the 3/8 in. O.D. stainless steel tube. The sample was held in place by a plug of loosely packed glass wool. Glass wool was also placed in the side unions of the reactor and held in place by 200 mesh stainless steel screen on either side of the union (Fig. 1). The reactor was pressure tested with helium gas for possible leaks and then evacuated for ten min. A heating tape was tightly wrapped around the entire horizontal section of the reactor. Three thermocouples were placed at three different locations to monitor the temperature uniformity of the reactor. Convective heat loss was minimized by wrapping an insulating tape on top of the heating tape. A second heating tape was then wrapped on the top vertical section of the reactor with a thermocouple monitoring the temperature.

The amount of solvent added to give a desired solvent density in the pre-evacuated reactor was measured by a buret connected to the solvent charge line. Solvent density was calculated from the measured volume of the reactor and the density of the solvent at room temperature. After charging the horizontal section

of the reactor with solvent the lower heating tape was turned on. The temperature was allowed to reach approximately 10°C above the desired value. The charge cylinder was evacuated and pressurized with helium gas to a pressure of 1100 psig. The solenoid valve was then pulsed for 1-1.5 s, thus pushing the coal sample into the heated solvent. The temperature controller was then lowered to give the desired steady state reaction temperature, which was usually reached in 1 to 2 min. At the same time, the upper heating tape was turned on to provide the same temperature to the vertical tube.

At a predetermined time heating was stopped, the insulation removed and the system allowed to cool to room temperature (temperature dropped 100°C in 5 min). Solvent and product were discharged into a flask at approximately -10°C. The reactor was then washed with pyridine until the effluent ran clear. To insure that no soluble product remained on any reactor surfaces, the reactor was washed again using the liquefaction solvent. In some cases the pyridine wash was left out. The system was then purged with helium for 10 min and evacuated for five min. The 3/8 in. reactor was disengaged from the system and weighed. The tube was stored in a desiccator containing CaSO_4 or P_2O_5 absorbent.

Weight loss data were obtained from the direct measurement of the residue removed from the reactor. Liquid products were centrifuged, filtered and then rotary evaporated. The distillate and evaporation residue were saved for further analysis.

B. Chemical Conversion of Incorporated Solvent

To provide a large amount of product for the study of chemical conversion of incorporated solvent, a one liter stirred Parr reactor vessel was used. The reactor was loaded with 47.6 g coal, then pressure tested with helium for possible leaks and evacuated. The amine (250 ml) was added by a buret. The Parr vessel was placed in a preheated heating jacket at 290°C for 5 hrs. The liquefaction solution was filtered and the filter cake washed with pyridine until the filtrate was clear. The filtrate was rotary evaporated and the two fractions (distillate and evaporation residue) were saved for further analysis. The distillate was recycled to the filtration unit as the washing solvent, then back to the rotary evaporator. Evaporation and filtration were performed in a closed loop to prevent solvent contact with air. (Amine was found to react with CO_2 , forming undesired products. This was also the reason pyridine was used as washing solvent.) Dried residue in the filtration funnel was weighed to obtain weight loss data. Weight loss data from the tubing bomb and Parr bomb reactors were consistent.

Chemical conversion of incorporated solvent was studied using a 0.75 in. o.d., 9.75 in. long 316 stainless steel batch reactor sealed by two caps. The reactor was loaded with a known amount of the tarry coal-derived product and the stripping solvent in a helium-filled glove box. For steam stripping experiments, 20.38 g of aqueous H_2SO_4 solution at pH 0.39 was added into the reactor with 1.64 g of the tarry liquefaction product. Solution volume was determined to maintain reactor pressure below 1500 psi at reaction temperature. The weight of the tarry sample was chosen so that the final pH value would be 3.0, assuming complete neutralization of incorporated amine by the acid. In methanol and ethanol stripping runs, solution volume was calculated to achieve supercritical conditions. By keeping the ratio of moles of solvent to sample weight the same in all runs, sample sizes used in methanol and ethanol runs were 0.64 g and 0.59 g, respectively. The reactor was placed in a preheated furnace at 271°C for 2.5 hrs, then cooled to room temperature. The extract and residue were separated by filtration. Steam run filtrate was further extracted three times using 6 ml toluene. The water fraction was titrated with NaOH solution to pH 11.03. A precipitate formed. After filtering, the water fraction was again extracted 3 times using 6 ml toluene. Filtrates from methanol and ethanol runs were rotary evaporated to flash off the stripping solvent until a constant condensate weight was obtained.

included PSOC1351, Ill. #6 seam, high volatile C bituminous; PSOC1405P, Upper Wyodak Seam, subbituminous B; and PSOC1406P, Kinnema Creek Seam, lignite. These minus 20 mesh samples were shipped in one pound cans filled with argon, then transferred into small vials under dry helium and stored in a helium-filled desiccator. A summary of the proximate and ultimate analyses for each coal is shown in Table 1.

It is assumed that water is completely removed by the solvent during liquefaction, i.e.,

$$\text{conversion to solvent extract} = \frac{\text{as received weight loss} - \text{moisture content}}{1 - \text{moisture content} - \text{ash content}} \\ (\text{daf, i.e., dry and ash free})$$

Since the primary interest is the conversion of organics in the coal to extracts, daf basis will be used in the subsequent discussion unless otherwise mentioned.

III. RESULTS AND DISCUSSION

A. Effect of Solvent Property

Dissolution of coal was found to be strongly dependent on the choice of the nitrogen containing solvent. Seven solvents with an assigned solvent property number were examined. The correlation of conversion and the assigned property number is illustrated in Figure 2. It is evident that as the number increases conversion also increases.

B. Effect of Temperature

Temperature is the most important processing variable in these studies. For example, in one of the selected amines the conversion of North Dakota lignite to solubles increased continuously from 60 percent at 220°C to 100 percent at 275°C (Figure 3). When compared with some other liquefaction solvents, such as recycle distillate cuts (Bockrath and Illig, 1984), 1,2,3,4-tetrahydroquinoline (Atherton and Kulik, 1982) and indole and indoline (Padrick et al. 1984), the amines chosen by us show an equal or higher conversion at considerably lower temperatures. This implies that reaction severity can be greatly reduced using the solvents we selected. Results of a comparative study of liquefaction in amine with vacuum pyrolysis and tetralin hydrolification, included in Figure 3, also suggest that the same or higher conversion can be obtained under very mild conditions using the solvents we selected. Figure 3 also shows that a sharp increase in reactivity took place between 230 and 250°C. This observation is consistent with the study of reaction time effect at different temperatures (Section III.F).

C. Effect of the Coal Rank

Figure 3 includes the liquefaction results of subbituminous and bituminous coals. While a complete dissolution of lignite (North Dakota coal) and subbituminous (Wyodak coal) was achieved at temperatures lower than 300°C, dissolution of the bituminous coal (Illinois #6 coal) was lower than the low rank coals. However, this was still much higher than dissolution in commonly used solvents. These results support speculation that interactions between oxygen functionals in the coal and the nitrogen solvent may be the governing factor in liquefaction at mild conditions (Atherton, 1984).

D. Effect of Solvent Density and Solvent-to-Coal Ratio

Solvent density was varied from 0.2 g/ml to 0.6 g/ml. Conversion to soluble materials appeared to be independent of the system density. In addition, solvent to coal ratio (s/c) did not appear to effect conversion when s/c was above 1/1 (w/w). Some of the North Dakota lignite conversion data shown in Figure 3 were obtained at a different density, but were found to fit the curve drawn for temperature effect at a constant density. It should be mentioned that solvent density changed from subcritical to supercritical within this density range. Therefore, since conversion is not dependent on density it could be implied that conversion is limited by chemical reactions.

E. Effect of Hydrogen

Figure 3 also shows data from liquefaction experiments with amine and hydrogen mixture. In the presence of hydrogen the same level of conversion can be achieved

while reducing the reaction temperature by 10°C.

F. Effect of Reaction Time

Since the process under study appeared to be governed by chemical reaction, the reactor system was modified to provide rapid heating and minimize non-isothermal effects (Fig. 1). These conditions facilitated the kinetic interpretation of experimental data. The conversion data were taken at three different temperatures, and at least three different reaction times for each temperature were studied.

Figure 4 shows data obtained at 230, 250 and 275°C at reaction times between 30 and 120 minutes. Conversion increased continuously with increasing time for all three temperatures. At 275°C complete dissolution of coal was observed in 90 min, while at lower temperatures the conversion is substantially lower. Conversion greater than (daf) 100% was observed. This phenomena may be due to dissolution of some ash (mineral matter) from the coal.

G. Process Chemistry

Figure 5 is a flow chart of one liquefaction experiment showing the subsequent product handling. Careful monitoring of stoichiometric balance was essential since mass balance is the first step in understanding chemical reactions and pathways. The chart also contains a number of analyses performed on selected samples.

1. Mass Balance

Reaction gases were collected from a tubing bomb liquefaction run and analyzed on a GC using 1/4 in. S.S. Chromosorb 102 column and an 1/8 in. S.S. molecular sieve column. Fig. 5 shows the analysis of a gas sample. From the identification of all the major gaseous products, it was determined that less than 1% of the carbon present in the coal was converted to these gases. Total gases produced were approximately 0.2% of the daf coal weight used for liquefaction. CO₂ was notably absent in the gas stream, having possibly reacted with the amine to form other compounds. The presence of NH₃ and butane in the gas product also indicated that the amine was hydrogenated and cleaved during liquefaction.

After collecting the gas sample the liquefaction residue was washed with fresh solvent. The resulting solution was centrifuged, filtered and rotary evaporated to obtain two distinct fractions. Selected solid samples were chosen for characterization. The residues produced in centrifugation and filtration steps were 1.68% and 2.2% of the as received coal, respectively. From energy dispersive X-ray analysis, the centrifuge residue contained high concentrations of calcium and silicon, as well as measurable amounts of Al, S, Fe, Cu, Mg and Ni.

2. Product Characterization

Following fractionation a set of characterization techniques, summarized in Fig. 5, were used to explore the governing chemistry. Two distinct fractions were obtained after rotary evaporation. One was black tarry material (solid products) and the other clear liquid (distillate). The solid sample's weight was 2.5 times that of the original daf coal, which indicates extensive solvent incorporation during liquefaction.

The pure solvent and the distillate fraction from evaporation were analyzed by GC (Fig. 6). The major liquefaction product in the distillate appears to be



The structure of the concentrated (through distillation) compound was established by GC/MS, IR, and ¹H NMR. Its presence suggests that amine attacks carbonyl groups in coal and may be a hydrogen source in liquefaction. This compound may be a key in evaluating solvent recovery processes. Solvent impurity peaks a and b have repeatedly been shown to have same retention time, Figure 6.

The tarry residue after evaporation was stored in a vacuum desiccator for 40 days at which time the solid, now fairly dry, reached a constant weight 1.39 times the original daf coal. The detailed desorption study is described later in this paper. After desorption the condensed tarry compound was characterized by sequential Soxhlet extraction, vapor pressure osmometry, elemental analysis, GC/MS, ^1H NMR, ^{13}C NMR and TGA. The results, discussed below, can also be compared with the previously reported analysis of tarry sample before 40 days storage (Chen and Kazimi, 1984).

In sequential Soxhlet extractions, the procedure developed by Mima, *et al.* (1976) was employed. The conversion of this solid product to oils, asphaltenes and preasphaltenes were 31.9%, 55.0% and 9.61%, respectively. Only 3.5% was pyridine insoluble. The average molecular weight of the tarry products, using vapor pressure osmometry, was about 610. Pyridine was used as solvent in the analysis.

Elemental analysis was performed on selected samples. These analyses showed that most oxygen and sulfur in lignite converts to liquid products in the distillate after rotary evaporation of the whole dissolved product (Fig. 5). This strengthens the theory that cleavage of oxygen functionals is critical in the early stage of coal liquefaction, and that nucleophilic solvents are very efficient in accomplishing this reaction.

Solvent incorporation can also be deduced from the nitrogen content of the solid product. As mentioned earlier, the solid product reached a constant weight 1.39 times that of the original daf coal after 40 days in *vacuo*. Assuming the weight gain, 0.39 g per 1 g of daf coal, was due to incorporated solvent in its original molecular form, then the nitrogen content of the solid product would be 6.39%. Direct elemental analysis showed 5.68% nitrogen content. The difference between the two numbers indicates that solvent condensation took place during liquefaction. In fact, a significant amount of NH_3 was present in the product gases.

In the ^1H NMR spectrum of the solid sample dissolved in dimethylsulfoxide, Figure 7, it is interesting to note that no clear aromatic hydrogen peaks appear around δ 7 or conjugated double bonds between δ 4.5 to 8. Similar results were also obtained when the sample was dissolved in D_5 -pyridine and CDCl_3 . This observation led us to perform a ^{13}C NMR analysis. A sharp peak around 120 ppm indicates the existence of aromatic carbon. The absence of aromatic hydrogen could imply that carbons at the outskirts of fused aromatic clusters were substituted during coal liquefaction in amine.

The thermogravimetric curve of the tarry product is shown in Figure 8. The sample was derived from the Parr reactor rather than the tubing bomb, differing mainly in the use of pyridine wash after liquefaction (see Experimental Section). The thermogravimetric analysis was performed in nitrogen with $20^\circ\text{C}/\text{min}$. heating rate. The thermogram indicates that the sample lost 50% of its weight below 300°C and all organics had been volatilized below 800°C .

H. Solvent Incorporation and Recovery

Evaporation of the pyridine washed and liquefaction amine washed samples produced a tarry product which had a weight 1.65 and 2.5 times the original daf coal weight, respectively. To measure the solvent recovery three different tests were conducted.

1. Washing with a Second Solvent

To measure the incorporated solvent, an amine other than the liquefaction solvent was used to wash the reactor. The combined liquefaction and washing solution was analyzed by GC. The analysis indicated that 0.59 g of the liquefaction solvent was consumed per 1 g daf coal. Generally 2.0 g of amine was used with 1.0 g of coal in liquefaction.

2. Physical Desorption

After rotary evaporation, the tarry product (2.5 times the daf coal weight) was stored in vacuo for desorption studies. From elemental analysis of this sample, the evaporated fraction was found to be rich in nitrogen-containing compounds. The desorption process follows the Langmuir equation (the rate of desorption is proportional to the amount of absorbed material):

$$Y = 1.001e^{-0.65t} + 0.166e^{-0.065t} + 1.390$$

where Y = sample weight/daf coal wt
t = time in days.

Y approached an asymptotic value, 1.390, which implied that 0.39 g solvent per 1 g daf coal was incorporated into the coal product. The presence of two exponential terms indicates that the solvent removal is a two step process. One may be the evaporation of a light or loosely held fraction (e.g., Van der Waal force-bonded) from a tarry matrix, while the other step may require the removal of a fraction which is heavier or more tightly bound.

3. Chemical Conversion of Incorporated Solvent

Coal liquefaction was reported to involve the cleavage of oxygen cross-links such as esters (van Bodegom, et al., 1984); therefore, it was speculated that solvent amine was incorporated into products as amide. Aqueous acid, ethanol, and methanol were employed to remove nitrogen containing species from coal derived products. Using this approach, amides might be converted into amines and carboxylic acids through nucleophilic substitution by water and alcohols. North Dakota lignite was used in this study because it has a very high oxygen content (24%, daf).

Figure 9 illustrates the sample handling flow chart and major analyses for the products derived from methanol stripping, which dissolved 52.4% of the tarry products. The solid residue was characterized by sequential Soxhlet extractions, vapor pressure osmometry (V.P.O.) and elemental analysis. Conversion of this solid product to hexane, benzene and pyridine solubles was 10.8, 8.6 and 55.7%, respectively, while 24.8% was pyridine insoluble. V.P.O. was used for determination of molecular weight, with pyridine as the solvent. The measured average molecular weight was 1951. The liquid phase after stripping was filtered and then evaporated under vacuum at 40°C. The resulting tarry fraction (0.55 g) was also characterized by sequential Soxhlet extractions, V.P.O. and elemental analysis. More than 92% of this tarry fraction was hexane soluble and it was completely dissolved in pyridine.

Material balance indicated that 63% of the nitrogen in the tarry liquefaction product was converted to extracts and 13% to the distillate fraction. Analyses of the distillate fraction by GC/MS and interpretation of the spectra are currently being performed. In ethanol stripping, similar results were obtained.

Figure 10 illustrates the sample flow chart in steam treatment. Only 15% of coal liquefaction products dissolved in steam, and based on the elemental analysis more than 39% nitrogen was removed from the coal liquefaction products. From V.P.O. analysis, the average molecular weight of steam treated products was 648, which is slightly higher than the tarry product before stripping. In sequential Soxhlet extractions, the conversion of hexane, benzene and pyridine was 41.7, 15.1 and 34.2%, respectively. Toluene extraction fractions and precipitation solids are currently under analysis.

The total solid products recovered after stripping with methanol, ethanol and steam were 92, 85 and 96%, respectively. In the calculation of alcohol stripping data, solids left in the stripping unit and evaporator were taken into consideration. It is worth mentioning that total asphaltene fraction decreased during stripping. From the Soxhlet extraction data of all three stripping products, it is clear that asphaltene converted to preasphaltene and pyridine-insolubles. Only a small fraction of asphaltene converted to oil in alcohol strippings. All

stripping products showed higher oxygen content, indicating that water and alcohol were involved in the reaction. We intend to perform IR analysis so that the specific pathway of oxygen functionals can be elucidated.

IV. CONCLUSIONS

Systematic study of coal liquefaction with amine continues to demonstrate the promise of the process under development. The following table compares some of our experimental results with those of a typical tetrahydroquinoline extraction (Atherton and Kulik, 1982)

	Amine (GSRI)	THQ
Temperature, °C	275	400
Pressure, psi	<500	1100
Gas Product, wt%	<1%	~10%
Conversion to Solubles (daf)	100%	95%
Product Undistillable at 500°C	~30%*	~80%†
Molecular weight of tarry product	610	--

*See Figure 8.

†Undissolved coal is included as undistillable.

We are particularly encouraged by the fact that the majority of the tarry product is distillable at 500°C. This suggests that the incorporated solvent is likely to be removed by distillation. Further development of the process requires a better understanding of process chemistry to determine 1) the governing chemical interactions between amines and coal and 2) the type of solvent recovered by physical separation or chemical conversion so that it can be recycled.

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1. The identities of the solvent are not disclosed in this paper because the patent application is pending. We plan to disclose this information at the ACS meeting.

Table 1. Properties of Coals Used in the Liquefaction Study

Sample	PSOC-1351	PSOC-1405P	PSOC-1406P
Rank	HVCB	SUBB	Lignite
Province	Interior	N. Gr. Plains	N. Gr. Plains
State	Illinois	Wyoming	N. Dakota
Moisture	8.08	18.82	29.64
Ash	10.56	7.15	8.23
Volatile matter	37.08	38.23	21.32
Fixed carbon	44.28	34.80	30.80
C, daf, %	76.26	74.44	67.72
H, daf, %	4.85	5.46	4.97
N, daf, %	1.32	1.34	1.40
S, daf, %	5.31	2.03	1.33
O, (% by diff.)	12.26	16.73	24.58
H/C (atomic)	0.76	0.88	0.88

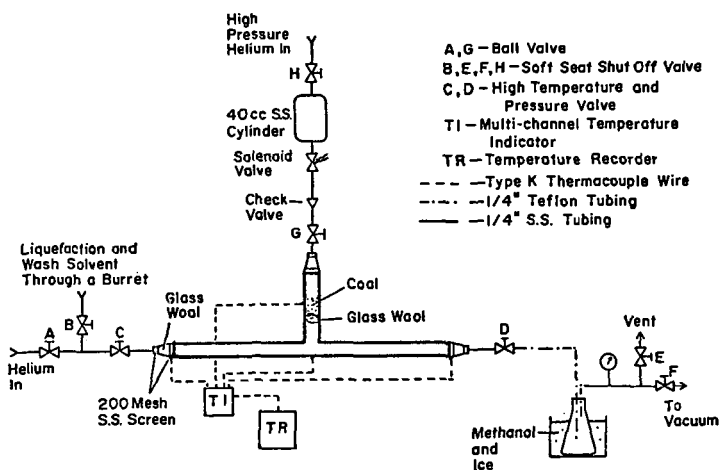


Figure 1. Experimental Arrangement

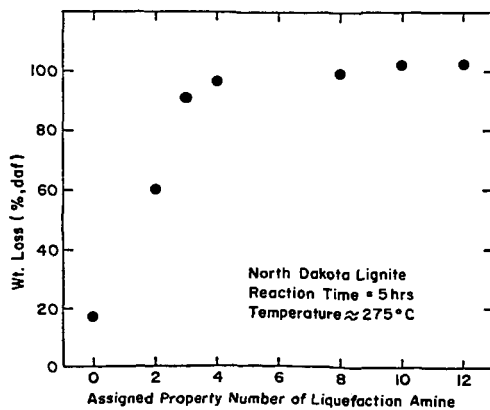


Figure 2. Property Number Effect

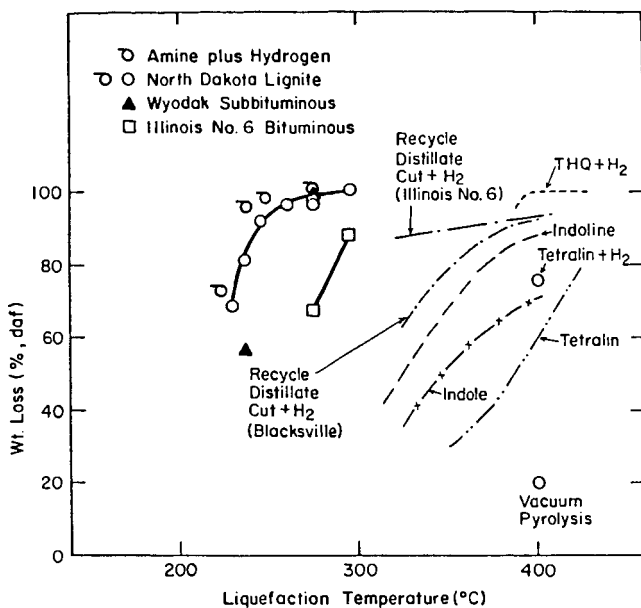


Figure 3. Effect of Temperature, Coal Rank and Hydrogen on Liquefaction Conversion. Symbols Represent GSRI Data, Broken Lines Represent Other Literature Data

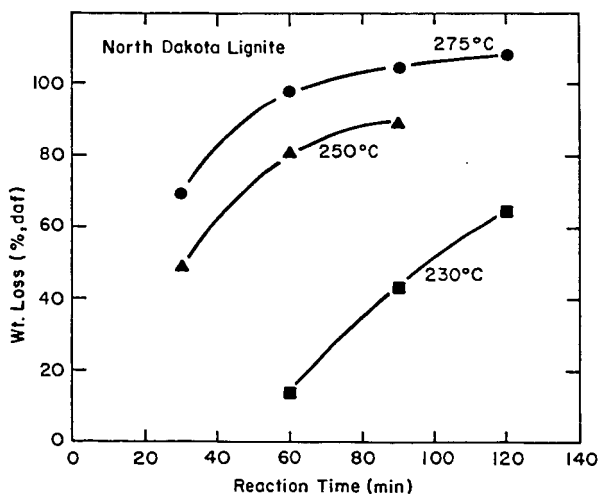


Figure 4. Reaction Time Effect

2.0 g North Dakota Lignite (as received)
2.0 g (2.7 ml) amine in 12.2 ml Reactor

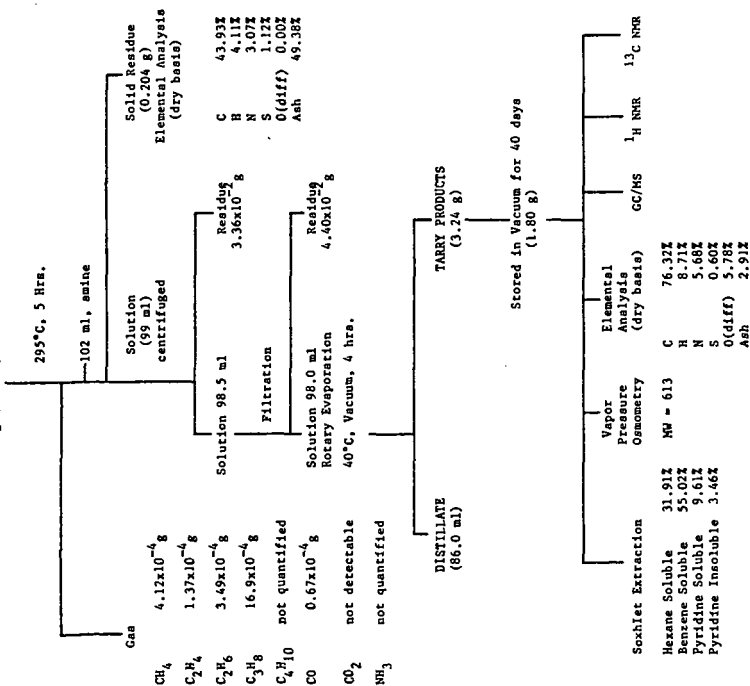


Figure 5. Liquefaction Flow Chart

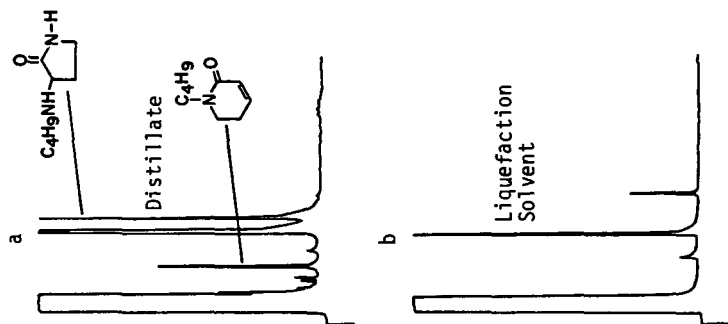


Figure 6. Chromatograms of Solvent and Distillate Fraction

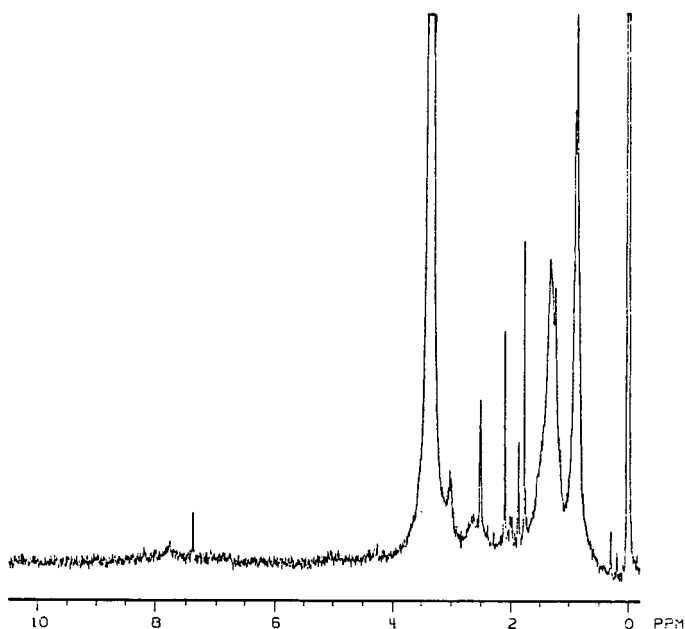


Figure 7. ^1H NMR Spectrum of Solid Products in Dimethylsulfoxide (Nicolet N-200)

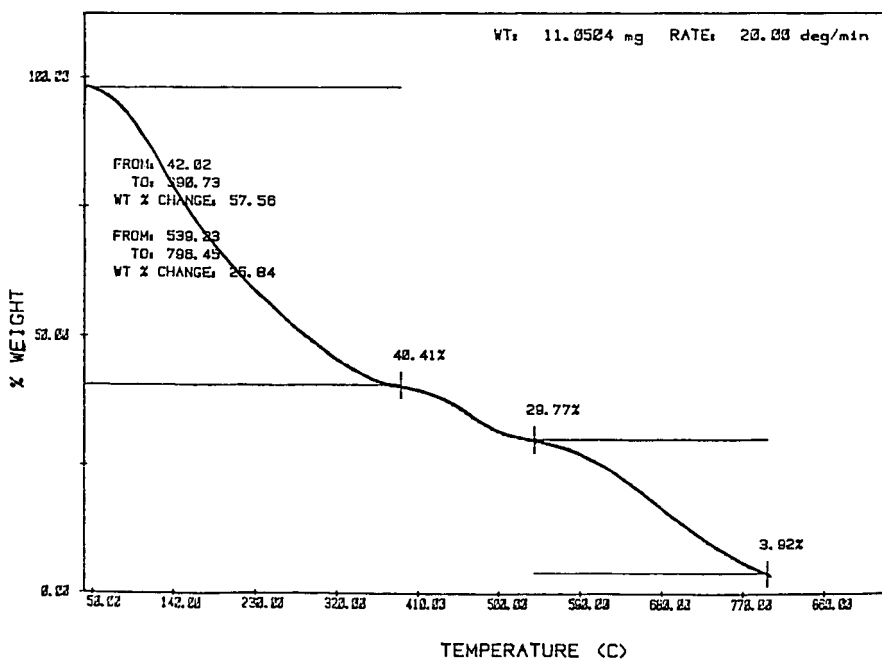


Figure 8. Thermogram of Solid Products

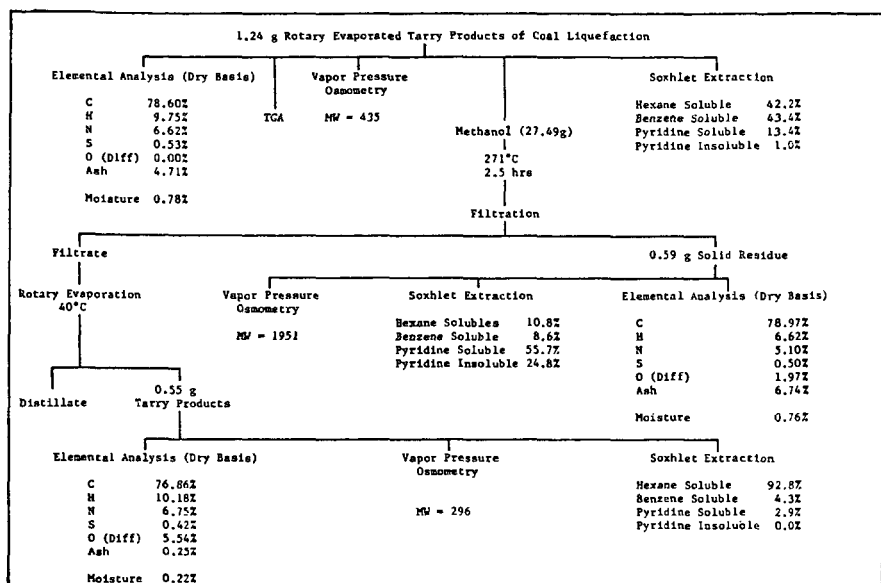


Fig. 9. Methanol Stripping and Related Products Characterization

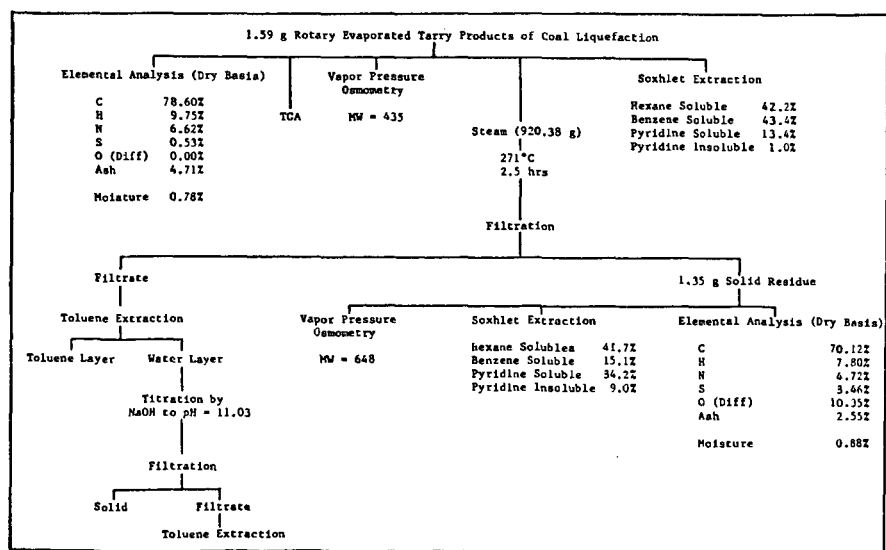


Fig. 10. Steam Stripping and Related Products Characterization